Efficient Conversion of Olefins into Epoxides, Bromohydrins, and Dibromides with Sodium Bromide in Water-Organic Solvent Electrolysis Systems

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Selective functionalizations of dimethyl 4-cyclohexene-1,2-dicarboxylate (1) and acyclic olefins **5** into the corresponding epoxides **2** and **6**, bromohydrins **3** and **7**, and 1,2-dibromides **4** and **8** were performed by electrolysis in a MeCN-H_2O-NaBr-(Pt) system. Lower Br^- concentration (less than 0.05 M) facilitates the formation of **2** in neutral medium and of **3** in acidic medium, whereas higher Br^- concentration (more than 1.5 M in acidic medium) produced exclusively **4**. The effective C-C bond cleavage of the epoxy group of **2**, leading to the corresponding diacetal **10**, was also accomplished by electrolysis in a MeOH-H_2SO_4-(C) system.

Epoxidation and halofunctionalization of olefins are essential techniques for the functionalization of complex molecules in synthetic organic chemistry. Interest in electrochemical epoxidation of olefins has been focused on the production of ethylene and propylene oxides in an aqueous sodium chloride or bromide solution.[1] However, associated with these electrolyses are difficulties in achieving product selectivity as well as obtaining high yields of the epoxides.[1a,b] In preliminary papers,[2] we reported a regioselective ω-epoxidation of polyisoprenoids promoted by sodium bromide during electrochemical oxidation in a MeCN-THF-H_2O-(Pt) system. Now we present a general procedure for the selective conversion of olefins into their epoxides, bromohydrins, or dibromides using sodium bromide in water-organic solvent electrolysis systems.

Most of the electrolyses of dimethyl 4-cyclohexene-1,2-dicarboxylate (1) as well as acyclic olefins **5** in water-organic solvent in the presence of halide salts were carried out in an undivided cell equipped with two Pt electrodes at a constant current of 3.3 mA/cm^2 (5 F/mol of electricity) at room temperature. The electrolysis of **1** in MeCN-H_2O (1/4)-NaBr system[3] afforded the epoxide **2** (Scheme I) in 97% yield (entry 1, Table I), while the electrolysis with NaCl and NaI did not give any desired products. The NaCl solution afforded mixed products, including the corresponding chlorohydrin, and the NaI solution resulted in the recovery of the starting olefin **1** (entries 2 and 3). These results are in contrast to that of the electrolysis of gaseous olefins in aqueous NaCl solution, which produces the corresponding epoxides with few by-products as compared to electrolysis in NaBr solution.[1c]

Interestingly, increase of the percent of acetonitrile from 20% to 80% suppresses significantly the formation of the epoxide **2**, and some dibromide **4** could be isolated (entry 4). The correlation between Br^- concentration and the yield of **2** is shown in Figure 1.

The electrolysis at lower Br^- concentration can provide the epoxide **2** preferentially, whereas at higher Br^- concentration the yield of **2** does not exceed 20%.[4] A similar electroepoxidation took place in 80% aqueous two-phase systems, e.g., hexane-H_2O, dimethoxyethane (DME)-H_2O, and CH_2Cl_2-H_2O (entries 5-7). Interestingly, aqueous 20% MeOH solution can also be used for this purpose, but in aqueous 80% MeOH, the electrolysis provided a complex mixture of **2** (8%) and **3b** (28%) (entries 8 and 9).

In acidic media, only the bromohydrin **3a** was obtained in place of the epoxide **2**. The selective formation of **3a** was accomplished by electrolysis at lower Br^- concentration, less than 0.05 M, under acidic conditins (entries 10 and 11). Increase of the Br^- concentration in the aqueous

Table I. Electrolysis of Dimethyl 4-Cyclohexene-1,2-dicarboxylate[a]

entry	solvent (mL/mL)	halide salts[b]	products, %[c] 2	3	4	% recovered 1
1	MeCN-H_2O (2/8)	NaBr	97			
2	MeCN-H_2O (2/8)	NaCl		24[d]		
3	MeCN-H_2O (2/8)	NaI				82
4	MeCN-H_2O (8/2)	NaBr	19		18	42
5	hexane-H_2O (2/8)	NaBr	87			
6	DME-H_2O (2/8)	NaBr	94			
7	CH_2Cl_2-H_2O (2/8)	NaBr	89			
8	MeOH-H_2O (2/8)	NaBr	80			
9	MeOH-H_2O (8/2)	NaBr	8	23		68
10	MeCN-H_2O (0.5/9.5)	HBr[e]		97		
11	MeCN-H_2O (0.5/9.5)	NaBr-H_2SO_4		72	3	
12	MeCN-H_2O (8/2)	NaBr[f]-H_2SO_4			92	
13	MeOH	NaBr[g]-H_2SO_4		88		

[a] Carried out by using two Pt electrodes (1.5 × 2 cm^2) at 3.3 mA/cm^2, passing 4-5 F/mol of electricity. [b] Twenty milligrams of the halide salts was used, unless otherwise noted. [c] Isolated yield. [d] Corresponding chlorohydrin. [e] Aqueous hydrobromic acid (0.03 mL). [f] Sodium bromide (250 mg) was added. [g] Portionwise addition of sodium bromide (6.2 mg, 3.1 mg; 10 times) every 20 min.

(1) (a) Ellis, K. G.; Jansson, R. E. W. *Chem. Ind. (London)* **1980**, 864. (b) Ibl, N.; Selvig, A. *Chem.-Ing.-Tech.* **1970**, *42*, 180. (c) Dietz, R.; Lund, H. "Organic Electrochemistry"; Baizer, M. M., Ed.; Marcel Dekker: New York, 1973; p 821. (d) Weinberg, N. L. "Technique of Electroorganic Synthesis"; Wiley: New York, 1974; Part I, p 368. (e) Weinberg, N. L; Weinberg, H. R. *Chem. Rev.* **1968**, *68*, 449

(2) (a) Torii, S; Uneyama, K.; Ono, M.; Tazawa, H.; Matsunami, S. *Tetrahedron Lett.* **1979**, 4661; (b) Torii, S.; Uneyama, K.; Matsunami, S. *J. Org. Chem.* **1980**, *45*, 16.

(3) A lower NaBr concentration (less than 0.1 M) in H_2O-MeCN-NaBr system provided seemingly a homogeneous solution, while a two-phase electrolysis system was obtained at higher NaBr concentration (more than 1.0 M in H_2O-MeCN, 1/4).

(4) Involving 1,2-dibromide **4** and 1,2-diol **10**.

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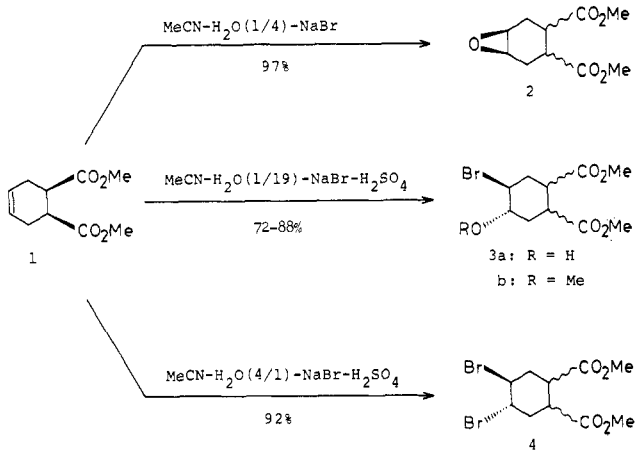
Scheme I



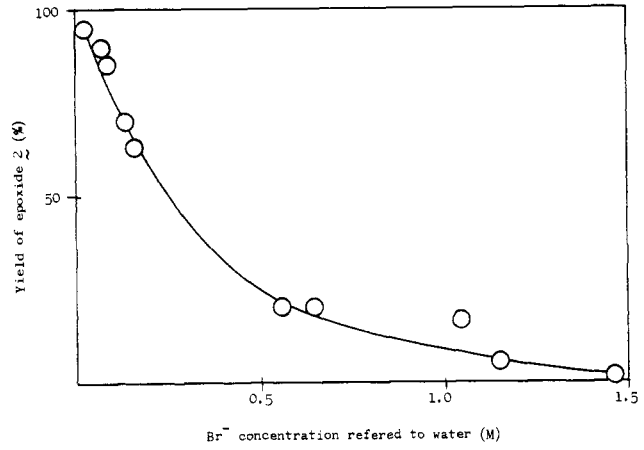


Figure 1. Electroepoxidation of 1 in the MeCN–H_2O–NaBr system. The electrolyses were carried out at a Br^- concentration of less than 0.55 M in MeCN–H_2O (1/4) and more than 0.55 M in MeCN–H_2O (4/1).

phase to more than 1.5 M by increasing the amount of bromide salt and/or decreasing the quantity of water in the electrolysis media facilitates the formation of 1,2-dibromide **4** (entry 12). Figure 2 shows the correlation between Br^- concentration and the distribution of the products **3** and **4** in acidic media. Thus, selective bromomethoxylation of **1** could be achieved by addition of NaBr throughout the electrolysis such that the Br^- concentration was kept at less than 0.05 M (entry 13).

These results show that the electrohalofunctionalization in water–organic solvent systems proceeds by different pathways depending on either the acidity of the electrolysis media or the Br^- concentration. The discharge of Br^- at the anode may generate bromine.[5] Thus, the higher Br^- concentration the bromine would distribute into the nonaqueous phase and react with olefin **1** to give 1,2-dibromide **4**. On the other hand, at lower Br^- concentration, the rapid hydrolysis of bromine in water produces HOBr,[5] which, in turn, moves to the organic phase and reacts with olefin to afford the bromohydrin **3a**. It is well-known that HOBr can rapidly decompose in neutral and acidic aqueous solutions.[5] But it is possible that the water–organic solvent electrolysis medium helps to minimize the decom-

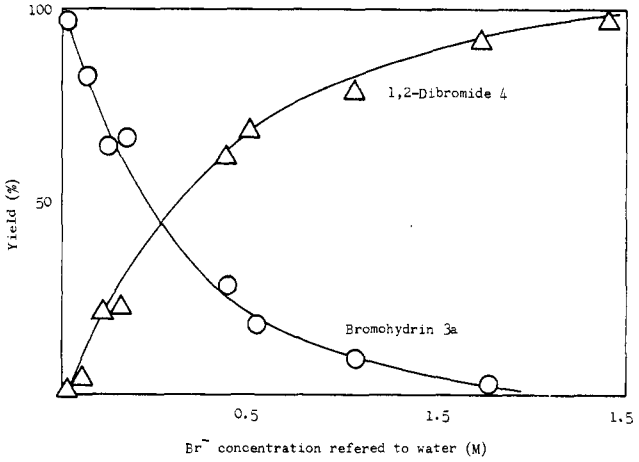
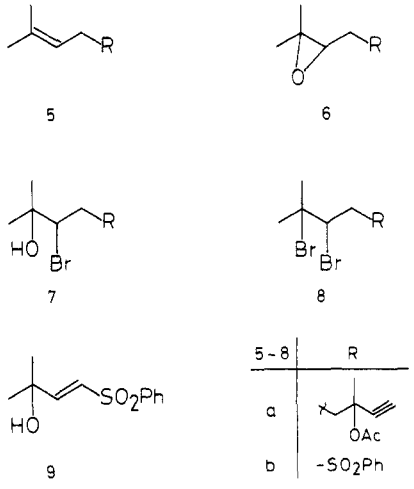


Figure 2. Electrochemical bromofunctionalization in the MeCN–H_2O–NaBr–H_2SO_4 system. The electrolyses were carried out at a Br^- concentration of less than 0.2 M in MeCN–H_2O (1/4) and more than 0.2 M in MeCN–H_2O (4/1).

Chart I



position of HOBr because of its diffusion into the nonaqueous layer.

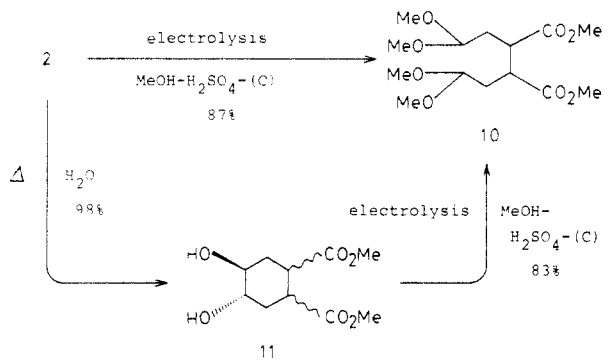
On the basis of the preceding results, we attempted the selective halofunctionalization of acyclic olefins **5** (see Chart I) by the same electrolysis procedure. Electrolysis of **5a** in the MeCN–H_2O (7/2)–NaBr (~0.08 M) system produced the epoxide **6a** in 82% yield. In contrast, the electrolysis of **5b** yielded **9** (100%), which could arise from bromohydrin **7b** by reaction with sodium hydroxide generated at the cathode.[5] On the other hand, the regioselective bromohydroxylation of **5a** proceeded smoothly by electrolysis in the MeCN–H_2O (7/2)–NaBr–formic acid system to give **7a** (93%). The conversion of **5b** into **7b** was accomplished in 81% yield when ammonium bromide was used as a supporting electrolyte in the same medium. The basicity of ammonium hydroxide would not be strong enough to promote the formation of **9**. At higher Br^- concentration, the addition of bromine to the olefins **5** took place preferentially, affording **8a** (94%) and **8b** (92%), respectively.

Straightforward electrolytic C–C bond cleavage of the epoxy group of **2** has also been observed, since the electrolysis of a solution of **2** in MeOH–H_2SO_4 system afforded diacetal **10** (87%), a precursor of 1,2,3,4-butanetetracarboxylic acid.[6] The electrolysis of the 1,2-diol **11** in the

(5) (a) Weinberg, N. L. "Technique of Electroorganic synthesis"; Wiley: New York, 1975; Part II, p 1. (b) Weinberg, N. L.; Hoffman, K. *Can. J. Chem.* **1971**, *49*, 740. (c) Vanleugenhaghe, C.; Valensi, G.; Pourbaix, H. "Atlas of Electrochemical Equilibrium in Aqueous Solutions"; Pourbaix M., Ed.; Pergamon Press: Oxford 1966; p 604. (d) Allen, M. J. "Organic Electrode Process"; Chapman and Hall: London, 1958; p 151; see also ref. 1.

(6) (a) Franz, J. E.; Knowles, W. A.; Osuch, C. *J. Org. Chem.* **1965**, *30*, 4328. (b) Lynn, J. W.; Roberts, R. L. *Ibid.* **1961**, *26*, 4303. (c) Hopff, H.; Rapp, W. U.S. Patent 2 203 628, **1940**.

Scheme II



$MeOH-H_2SO_4$ system also gave **10** as a sole product (83%). (See Scheme II).

In comparison with the reported procedure[7] on the electrochemical C–C bond cleavage of 1,2-diols and epoxides using MeOH–Et_4NOTs–(C) system, the present $MeOH-H_2SO_4$–(Pt) procedure represents a remarkable improvement in product selectivity as well as the isolated yield of the diacetal **10**.[8]

Experimental Section

Boiling points and melting points are uncorrected. Infrared spectra were recorded on a JASCO IRA-1 spectrometer. ^1H NMR spectra were recorded at 60 MHz on a Hitachi R-24 instrument and the chemical shifts are reported in parts per million (δ) downfield from internal Me_4Si. Elemental microanalyses were performed in this laboratory.

Materials. Dimethyl 4-cyclohexene-1,2-dicarboxylate (**1**),[9] dehydrolinalyl acetate (**5a**)[10], and prenyl sulfone (**5b**)[11] were prepared according to the procedures described in the literature.

Electrolysis Apparatus. Electrolysis was carried out in a beaker, 3 cm in diameter and 10 cm high, fitted with two smooth platinum foil electrodes (1.5 × 2 cm^2) 5 mm apart. Regulated dc power was supplied by a Metronix 543B instrument. Unless otherwise noted, 4–5 F/mol of electricity was passed at 20–25 °C.

Electroepoxidation of Dimethyl 4-Cyclohexene-1,2-dicarboxylate (1). A mixture of **1** (40 mg, 0.2 mmol) and NaBr (20.4 mg, 0.2 mmol) in MeCN (2 mL)–H_2O (8 mL) was electrolyzed under a constant current density of 3.3 mA/cm^2 for 2.7 h. The mixture was extracted with ether (3 × 5 mL), and the extracts were washed with brine and dried (Na_2SO_4). After evaporation of the solvents, the residue was chromatographed (SiO_2; benzene/AcOEt, 4/1) to give epoxide **2** (41.8 mg, 97%), whose IR and ^1H NMR spectra were identical with those of an authentic sample.[9]

Electrobromohydroxylation of 1. A mixture of **1** (46.4 mg, 0.234 mmol) and aqueous 47% HBr (0.03 mL, 0.51 mmol) in MeCN (0.5 mL)–H_2O (9.5 mL) was electrolyzed at 3.3 mA/cm^2 for 3.14 h. The mixture was extracted with ether and worked up in the usual manner. The crude products were chromatographed (SiO_2; benzene/AcOEt, 4/1) to give 67 mg (97%) of **3a**[12]: IR (neat) 3420 (OH), 1730 cm^{-1} (C=O); ^1H NMR (CCl_4) δ 1.8–3.4 (m, 6 H), 3.70 (s, 6 H, CH_3O), 3.75–4.30 (m, 2 H, HCBr, HCOH).

Electrobromomethoxylation of 1. A mixture of **1** (55.8 mg, 0.28 mmol) and NaBr (6.2 mg, 0.06 mmol) in MeOH (10 mL) containing concentrated H_2SO_4 was electrolyzed at 3.3 mA/cm^2 for 3.8 h. In the course of the electrolysis, additional NaBr (10 × 3.1 mg, total 0.3 mmol) was added every 20 min. The resulting mixture was poured into aqueous $NaHCO_3$ and worked up. Column chromatography (SiO_2; benzene/AcOEt, 4/1) of the crude products yielded **3b**: 76.5 mg (88%); IR (neat) 1745 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 1.5–3.37 (m, 6 H), 3.37, 3.46, (s, 3 H, CH_3O), 3.72 (s, 6 H, CH_3OCO), 3.8–4.1 (m, 1 H, HCO), 4.1–4.5 (m, 1 H, HCBr).

Anal. Calcd for $C_{11}H_{17}BrO_5$: C, 42.74; H, 5.54. Found: C, 42.50; H, 5.42.

Electrobromination of 1. A mixture of **1** (43 mg, 0.217 mmol) and NaBr (250 mg, 2.42 mmol) in MeCN (8 mL)–H_2O (2 mL) was electrolyzed at 3.3 mA/cm^2 for 2.9 h. After addition of aqueous $NaHCO_3$ to adjust the pH value at 7, the mixture was worked up. Chromatography (SiO_2; benzene/AcOEt, 4/1) of the crude product gave **4** (71 mg, 92%), whose IR and ^1H NMR spectra were identical with those of an authentic sample.[13]

Electroepoxidation of Dehydrolinalyl Acetate (5a). A mixture of **5a** (30 mg, 0.154 mmol) and NaBr (16 mg, 0.155 mmol) in MeCN (7 mL)–H_2O (2 mL) was electrolyzed at 7 mA/cm^2 for 50 min. The usual workup followed by column chromatography (SiO_2, hexane/AcOEt, 7/1) gave **6a**: 26.6 mg (82%); bp 76–79 °C (2.2 mm); IR (neat) 3260, (C≡CH), 1745 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 1.30 (s, 3 H, CH_3), 1.32 (s, 3 H, CH_3), 1.71 (s, 3 H, CH_3), 2.04 (s, 3 H, CH_3), 2.20–1.60 (m, 4 H, CH_2), 2.56 (s, 1 H, C≡CH), 2.75 (t, J = 5.2 Hz, 1 H, HCO).

Anal. Calcd for $C_{12}H_{18}O_3$: C, 68.51; H, 8.72. Found: C, 68.55; H, 8.63.

Similarly, electrolysis of **5b** in NaBr (29.4 mg, 0.286 mmol)–MeCN (1.5 mL)–H_2O (7.5 mL) solution at 10 mA/cm^2 for 2.1 h gave **2-methyl-4-(phenylsulfonyl)-3-buten-2-ol (9)**: 32.3 mg (100%); mp 98–99 °C (from hexane/AcOEt, 4/1); IR (Nujol) 3438 (OH), 1300, 1280, 1140, cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.37 (s, 6 H, CH_3), 1.80 (s, 1 H, OH), 6.53 (d, J = 15 Hz, 1 H, HC=C), 7.10 (d, J = 15 Hz, 1 H, HC=C), 7.32–7.92 (m, 5 H, Ph).

Anal. Calcd for $C_{11}H_{14}O_3S$: C, 58.39; H, 6.24. Found: C, 58.10; H, 6.13.

Electrosynthesis of 3-Acetoxy-6-bromo-7-hydroxy-3,7-dimethyl-1-octyne (7a). A mixture of **5a** (30 mg, 0.154 mmol), NaBr (16 mg, 0.155 mmol), and formic acid (36 mg, 0.782 mmol) in MeCN (7 mL)–H_2O (2 mL) was electrolyzed at 7 mA/cm^2 for 0.83 h. The usual workup followed by column chromatography (SiO_2; hexane/AcOEt, 7/1) afforded **7a**: 41.5 mg (93%); bp 85–89 °C (2.6 mm); IR (neat) 3440 (OH), 3280 (HC≡C), 1740 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 1.37 (s, 3 H, CH_3), 1.39 (s, 3 H, CH_3), 1.71 (s, 3 H, CH_3), 2.04 (s, 3 H, CH_3CO), 1.77–2.39 (m, 4 H, CH_2), 2.57 (d, J = 1 Hz, 1 H, HC≡C), 3.92–4.11 (m, 1 H, HCBr).

Anal. Calcd for $C_{12}H_{19}BrO_3$: C, 49.24; H, 6.78. Found: C, 49.50; H, 6.58.

3-Bromo-2-methyl-4-(phenylsulfonyl)-2-butanol (7b). A mixture of **5b** (30 mg, 0.143 mmol) and NH_4Br (28 mg, 0.286 mmol) in MeCN (7.5 mL)–H_2O (1.5 mL) was electrolyzed at 10 mA/cm^2 for 2.1 h. The usual workup followed by column chromatography (SiO_2; ether/AcOEt, 1/1) gave **7b**: 35.6 mg (81%); IR (neat) 3476 (OH), 3056, 1305, 1150 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.32 (s, 3 H, CH_3), 1.38 (s, 3 H, CH_3), 2.04 (s, 1 H, OH), 3.65 (dd, J = 16, 8 Hz, 1 H, CH_2), 3.93 (dd, J = 16, 2 Hz, 1 H, CH_2), 4.24 (dd, J = 8, 2 Hz, 1 H, CH), 7.45–8.02 (m, 5 H, Ph).

Anal. Calcd for $C_{11}H_{15}BrO_3S$: C, 43.01; H, 4.92. Found: C, 43.25; H, 5.21.

3-Acetoxy-6,7-dibromo-3,7-dimethyl-1-octyne (8a). A mixture of **5a** (30 mg, 0.154 mmol) and NaBr (200 mg, 1.94 mmol) in MeCN (9.5 mL)–H_2O (0.5 mL) was electrolyzed at 10 mA/cm^2 (13 F/mol of electricity) for 1.7 h. The usual workup and subsequent column chromatography (SiO_2; hexane/AcOEt, 7/1) afforded **8a**: 50 mg (94%); bp 82–84 °C (2.3 mm); IR (neat) 3280 (HC≡C), 1745 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.74 (s, 3 H, CH_3), 1.84 (s, 3 H, CH_3), 2.00 (s, 3 H, CH_3), 2.06 (s, 3 H, CH_3CO), 1.60–2.20 (m, 4 H, CH_2), 2.58 (s, 1 H, HC≡C), 4.17 (m, 1 H, HCBr).

Anal. Calcd for $C_{12}H_{18}Br_2O_2$: C, 40.99; H, 5.22. Found: C, 40.70; H, 5.12.

2,3-Dibromo-3-methyl-1-(phenylsulfonyl)butane (8b). A mixture of **5b** (30 mg, 0.143 mmol) and NH_4Br (140 mg, 1.43 mmol) in MeCN (9 mL)–H_2O (0.2 mL) was electrolyzed at 5 mA/cm^2 (25 F/mol of electricity) for 6.4 h. The usual workup

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(8) Electrolysis of epoxide **2** in a MeOH–Et_4NOTs–(C electrodes) system [7] afforded a mixture of diacetal **10** (29%) and the corresponding monoacetal (34%). Electrolysis of 1,2-diol **11** in the same media afforded **10** (24%) and the monoacetal (25%).

(9) Cerefice, S. A.; Fields, E. K. *J. Org. Chem.* **1976**, *41*, 355.

(10) Saucy, G.; Marbert, R.; Lindlar, H.; Isler, O. *Helv. Chim* Acta **1959**, *42*, 1945.

(11) Juria, M.; Guy-Pouault, A. *Bull. Soc. Chim. Fr.* **1967**, 1411.

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(13) Klein, J.; Dunkelblum, E. *J. Org. Chem.* **1971**, *36*, 142.

followed by column chromatography (SiO_2; hexane/AcOEt, 5/1) gave **8b**: 48.5 mg (92%); mp 82–84 °C, IR (Nujol) 3055, 1312, 1160 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.75 (s, 3 H, CH_3), 1.95 (s, 3 H, CH_3), 3.71 (dd, J = 15, 9 Hz, 1 H, CH_2) 4.29 (dd, J = 15, 2 Hz, 1 H, CH_2), 4.51 (dd, J = 9, 2 Hz, 1 H, CH), 7.46–8.08 (m, 5 H, Ph).

Anal. Calcd for $C_{14}H_{14}Br_2O_2S$: C, 35.70; H, 3.81. Found: C, 35.99; H, 3.73.

Electrochemical Conversion of Dimethyl 4,5-Epoxycyclohexane-1,2-dicarboxylate (2) into Dimethyl 2,3-Bis(2,2-dimethoxyethyl)succinate (10). A mixture of **2** (150 mg, 0.70 mmol) and H_2SO_4 (0.15 mL) in MeOH (10 mL) was electrolyzed at 17 mA/cm^2 by using two glassy carbon electrodes (1.5 × 2 cm^2) for 6.75 h. Usual workup gave **10**: 187 mg (87%); IR (neat) 1725 (C=O), 1260, 1160, 1130, 1070, 955 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.40–2.32 (m, 4 H), 2.60–2.89 (m, 2 H, HCC=O), 3.31 (s, 12H, CH_3O), 3.72 (s, 6 H, CH_3OCO), 4.38 (t, J = 6 Hz, 2 H, OCHO).

Anal. Calcd for $C_{14}H_{26}O_8$: C, 52.16; H, 8.13. Found: C, 51.88; H, 8.34.

Hydrolysis of Dimethyl 4,5-Epoxycyclohexane-1,2-dicarboxylate (2). A suspension of **2** (500 mg, 2.33 mmol) in H_2O (50 mL) was heated to reflux for 3 h. The usual workup yielded **11** (531 mg, 98%).[9]

Electrochemical Cleavage of Dimethyl 4,5-Dihydroxycyclohexane-1,2-dicarboxylate (11). A mixture of **11** (103 mg, 0.44 mmol) and H_2SO_4 (0.15 mL) in MeOH (10 mL) was electrolyzed at 10 mA/cm^2 for 7.3 h by using two glassy carbon electrodes (1.5 × 2 cm^2). The usual workup gave **10** (119 mg, 83%), which was identifical in all respects with **10** obtained above.

Registry No. **1**, 4841-84-3; **2**, 51349-92-9; **3a**, 77743-51-2; **3b**, 77743-52-3; **3** chlorohydrin, 77743-53-4; **4**, 77841-42-0; **5a**, 29171-21-9; **5b**, 15874-80-3; **6a**, 77743-54-5; **7a**, 77743-55-6; **7b**, 77743-56-7; **8a**, 77743-57-8; **8b**, 77743-58-9; **9**, 77743-59-0; **10**, 77743-60-3; **11**, 61825-80-7; NaBr, 7647-15-6.

Ring Enlargement by [2,3] Sigmatropic Rearrangement of Cyclic Sulfonium Ylides. 2. Conformational Control of Product Stereochemistry

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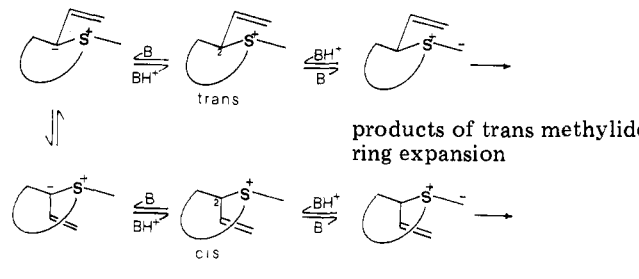
The geometry of the cyclic homoallylic sulfides produced by [2,3] sigmatropic ring enlargement of cyclic sulfonium ylides[5] is largely determined by configurational and conformational factors. Thus "trans" ylides (vinyl and S^+–CH_2^- moieties on opposite sides of the ring) can only attain a transoid transition state and rearrange to *E* products exclusively. "Cis" ylides, on the other hand, may attain both a cisoid and a transoid transition state whose relative energy depends on conformational factors which may be assessed merely by inspection of the ground state. Thus it is possible to direct the rearrangement toward one or the other steric course by appropriate substitutions on the ring or on the appended vinyl group. Wherever the sulfonium salt precursor has a H atom at the α allylic position, a certain extent of stereochemical control may be achieved by the method of ylide generation. Under "reversible" conditions (*t*-BuOK in THF/*t*-BuOH) the ring-expanded product largely arises from the "cis" ylide,[8] while under "irreversible" conditions (lithium diisopropylamide in THF) the product merely reflects the diastereoisomer population of the starting sulfonium salts, where the trans isomer often prevails.

Allylic sulfonium ylides rearrange to homoallylic sulfides in a concerted [2,3] sigmatropic process occurring via a five-membered transition state.[1] The geometry of the newly formed double bond is of interest. In acyclic systems there appears to be a strong preference for formation of the *E* olefin,[1b,2] a tendency which has been explained in terms of the conformational requirements of the R group:[3]

Because of its relative bulk, R will tend to set itself equatorial in the envelope conformation of the five-center transition state and end up trans to the substituent carrying the thioether group in the product olefin.[3]

When the S–C_2 bond is part of a ring,[4] however, the geometrical properties of the latter (configuration and conformation), as well as the properties (strain) of the product ring, may be expected to play a key role in determining the geometry of the cyclic olefin product.[6]

Scheme I



The study of the stereochemistry of the sulfonium ylides' ring enlargement is complicated by the sulfonium salt precursors existing as diastereomeric cis–trans pairs which, under the conditions required for ylide generation, may

(1) (a) Baldwin, J. E.; Hackler, R. E.; Kelly, D. P. *J. Chem. Soc., Chem. Commun.* **1968**, 538. (b) Evans, D. A.; Andrews, G. C. *Acc. Chem. Res.* **1974**, *7*, 147 and references therein.

(2) (a) Baldwin, J. E.; Patrick, J. E. *J. Am. Chem. Soc.* **1971**, *93*, 3556. (b) Grieco, P. A. *J. Chem. Soc., Chem. Commun.* **1972**, 702. (c) Grieco, P. A.; Boxler, D.; Hirsi, K. *J. Org. Chem.* **1973**, *38*, 2572.

(3) Trost, B. M.; Melvin, L. S., Jr. "Sulfur Ylides"; Academic Press: New York, 1975; Chapter 7.

(4) The [2,3] sigmatropic rearrangement of cyclic sulfonium ylides brings about a three-carbon ring expansion, leading to thiacycloalk-4-enes.[5]

(5) Vedejs, E.; Hagen, J. P. *J. Am. Chem. Soc.* **1975**, *97*, 6878.

(6) Indeed, for six-membered ammonium ylides Vedejs and co-workers have brought to light dramatic evidence of the effects that relatively minor structural changes in the starting material may have on the geometry of the ring-expanded product.[7]

(7) (a) Vedejs, E.; Arco, M. J.; Renga, J. M. *Tetrahedron Lett.* **1978**, 523. (b) Vedejs, E.; Arco, M. J.; Powell, D. W.; Renga, J. M.; Singer, S. P. *J. Org. Chem.* **1978**, *43*, 4831.

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